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Evaluation of beech for production of bio-char, bio-oil and gaseous materials

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ABSTRACT

Evaluation of Oriental beech (*Fagus orientalis* L.) was investigated with aspect of thermochemical conversion to obtain bio-char, bio-oil and gaseous. When the pyrolysis temperature increased, the bio-char yield decreased. A high temperature and smaller particles increase the heating rate resulting in a decreased bio-char yield. The bio-char obtained are carbon rich, with high heating value and relatively pollution-free potential solid biofuel. The liquefaction yield sharply increased with increasing the temperature near critical temperature and after that. In the pyrolysis, increases of liquid yields are considerably sharply for all of the samples with increasing of pyrolysis temperature from 690 K to 720 K. The beechnut oil was converted to biodiesel in supercritical methanol without using the catalyst. Experiments have been carried out in an autoclave at 493, 523 and 593 K, and with molar ratios of 1:6–1:40 of the oil to methanol. The yield of alkyl ester increased with increasing the molar ratio of oil to alcohol.

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1. Introduction

The basic structure of all woody biomass consists of three organic polymers: cellulose, hemicelluloses, and lignin in the trunk, foliage, and bark. Three structural components are cellulose, hemicelluloses and lignin which have rough formulae as $CH_{1.67}O_{0.83}$, $CH_{1.64}O_{0.78}$, and $C_{10}H_{11}O_{3.5}$, respectively (Demirbas, 2000a, 2001). The woody biomass also consists of extractives and minerals or ash.

The utilization of biomass via thermochemical conversion has received increased attention due to pressure to satisfy the increasing global energy demand and the decrease of environmental pollution (Demirbas, 1998; Tekin and Karagoz, 2013; Tekin et al., 2013). Three main biomass conversion processes are thermal, chemical and biochemical.

Thermal biomass conversion does include a number of possible roots to produce from the initial biorenewable feedstock useful fuels and chemicals. Thermal conversion processes include three sub-categories: combustion, gasification, pyrolysis and liquefaction. Torrefaction is one of the processes as well but can be categorized as a mild form of pyrolysis. Biorenewable feedstocks can be used as a solid fuel, or converted into liquid or gaseous forms for the production of electric power, heat, chemicals, or gaseous and liquid fuels (Gercel and Gercel, 2007; Demirbas, 2008a, 2008b, 2008c; Gonzalez et al., 2008). Fig. 1 shows the biomass thermal conversion processes (Demirbas, 2009).

Liquefaction processes result in liquid product, which can be easily stored and transported and require lower process temperatures (Mohan et al., 2006). The pyrolysis of biomass has been studied with the final objective of recovering a biofuel with medium-low calorific power (Frederick et al., 1994; Raveendran and Ganesh, 1996; Bridgwater et al., 1999; Font et al., 1999; Babu and Chaurasia, 2003). Wood and other forms of biomass are some of the main renewable solid energy resources available and provide the only source of liquid, gaseous and solid fuels (Demirbas, 2007).

Oriental beech (*Fagus orientalis* Lipsky) belongs to the Beech family (*Fagaceae*) and is closely related to its European counterpart (*Fagus sylvatica* Lipsky) (Gömöry et al., 1994). It is a large

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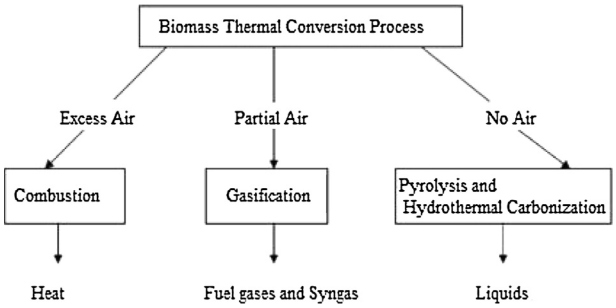

Fig. 1 – Biomass thermal conversion process modified from Demirbas (2001).

tree, normal mean heights in Turkey are 30 m but it can reach heights of up to 50 m.

Beech fruit is a pyramidal nut (beechnut or mast/beechmast), with a triangular section and about 1.5 cm in length, enclosed in spiky cupules. The cupules open by valves, which are one more than fruit number. The small triangular beechnuts are borne in pairs inside a cup with four prickly brown sides and change from green to brown as they ripen. The endocarp is a thick, smooth and shiny dark brown, hairy inside husk. Its color lightens as the beechnut dries. The husks then blow open by the wind and the nuts fall to the ground.

The fruit is a small, sharply 3-angled nut 10–15 mm long, borne in pairs in soft-spined husks 1.5–2.5 cm long, known as cupules. The nuts have high oil content. Beech oil is the oil expressed from the nuts of the beech tree.

Vegetable oils and their derivatives, especially (m)ethyl esters, commonly referred to as biodiesel. Methyl and ethyl esters of vegetable oils have several outstanding advantages among other new-renewable and clean engine fuel alternatives (Balat, 2005). Biodiesel is generally made of methyl esters of fatty acids produced by the transesterification reaction of triglycerides with methanol in the presence alkali as a catalyst (Clark et al., 1984; Bala, 2005).

Mostly biodiesel is derived from the vegetable oils using NaOH or KOH catalytic transesterification methanol process (Ma and Hanna, 1999). The purpose of the transesterification process is to lower the viscosity of the oil. Transesterification is the reversible reaction of a fat or oil with an alcohol (methanol or ethanol) to form fatty acid alkyl esters and glycerol. It can be alkali-, acid-, or enzyme-catalyzed; however, currently the majority of the commercialized technology resides in transesterification using alkali catalyzed reaction (Ma and Hanna, 1999). The transesterification occurs in supercritical methanol. The reaction can also take place without the use of a catalyst under conditions in which the alcohol is in a supercritical state (Saka and Kusdiana, 2001a; Demirbas, 2002a, 2002b, 2002c). Since supercritical methanol is hydrophobic with a lower dielectric constant, non-polar triglycerides can be well solvated with supercritical methanol to form a single phase oil/alcohol mixture (Saka and Kusdiana, 2001b; Warabi et al., 2004).

Pyrolysis proceeds in three steps. In an initial step, there is moisture and some volatile loss (Eq. (1)). Primary bio-char occurs in the secondary step (Eq. (2)). The last fast step follows by a slower step including some chemical rearrangement of the bio-char. During the third stage, the bio-char decomposes at a very slow rate and carbon-rich residual solid forms. The formation of secondary charring (Eq. (3)) makes the char less reactive.

$$\text{Biomass} \rightarrow \text{Water} + \text{Unreactedsolidresidue}, \tag{1}$$

$$\text{Unreactedsolidresidue} \rightarrow (\text{Volatile} + \text{Gases})1 + (\text{Char})1, \text{ and} \tag{2}$$

$$(\text{Char})1 \rightarrow (\text{Volatile} + \text{Gases})2 + (\text{Char})2. \tag{3}$$

This study is devoted to obtain liquid products from beech wood via alkali glycerol liquefaction and pyrolysis processes. Oil samples obtained from the beechnuts have been converted to their methyl esters (biodiesel) by transesterification in compressed methanol. Some fuel properties of the biodiesel were determined and compared with the biodiesel fuel specifications so as to define whether they were of fuel quality or not.

2. Experimental

2.1. Samples used

The wood and beechnut samples from Oriental beech (*F. orientalis*) trees used in the experimental studies were taken from the Eastern Black Sea region in Turkey approximately 40°39′ northern latitude at an altitude of 900 m. The trees were 35–55 years old. Before experiments the air dried wood samples with 5% moisture were chipped and then ground in a Thomas-Wiley mill to pass between 0.12 mm and 0.40 mm screen opening.

Oil was recovered from air dried and milled beechnut by hexane extraction. The oil samples were used in the experiments without further purification.

2.2. Structural and chemical analyses

For structural analyses, the wood samples were prepared according to TAPPI standard (TAPPIT 11 m-45). The percent lignin and percent extractives of the ground sample were determined. The ground sample was extracted with ethanol–benzene according to ASTM, and the lignin was determined as the insoluble residue after hydrolysis with 72% sulfuric acid.

The chemical analyses of the samples were carried out according to the ASTM D1103-80 and ASTM D1104-56 standard test methods.

2.3. Liquefaction in alkaline glycerol

Wood meal and anhydrous glycerol containing the appropriate amount of alkali (Na_2CO_3) were put into a round bottom distilling flask with two cylindrical standard ground joint necks. To the flask was attached a Liebig condenser with two standard ground joints NS cones of 75° angle connecting tubes. The temperature was measured with a mercury type thermometer (upper limit of reading being 673 K) which was attached to one neck of the distilling flask. Then the flask was immersed into a used vegetable oil bath. Products from wood meal passing into the condenser were collected in an Erlenmeyer flask at atmospheric pressure. The required liquefaction time of wood meal as described was about 15–20 min.

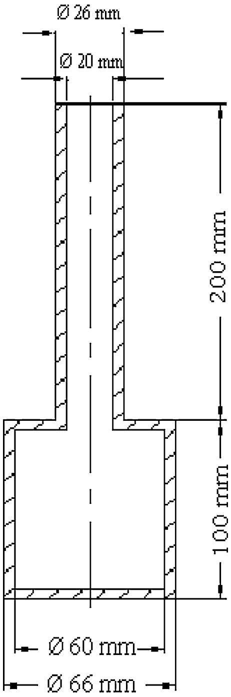

Fig. 2 – The pyrolysis tube reactor.

The liquid products from wood meal were fractionated into water solubles, water insolubles and solid residue.

2.4. Bio-oil via pyrolysis

The pyrolysis experiments were carried out in a stainless steel tube reactor (Fig. 2). The simple thermocouple (NiCr—constantan) was placed directly in the pyrolysis medium for temperature control. For each run, the heater was started at 298 K and terminated when the desired temperature.

The pyrolysis products from different heating rate runs were collected within three different groups as non-condensable gaseous products, condensable liquids products (bio-oil) and solid residue (bio-char). Following pyrolysis the liquid products were collected in a series of traps maintained at about 273 K and the organic part of the oil phase which dissolved in benzene was extracted in a rotary evaporator and the quantity of bio-oil was established. The higher heating values (HHVs) of bio-oil and bio-char from the samples in relation to the pyrolysis temperature were determined by bomb calorimeter according to the ASTM D2015 standard method.

2.5. Supercritical methanol transesterification

The experiments of the supercritical methanol transesterification of beechnut oil samples were performed in a laboratory scale apparatus. The main element of this device was a vertical cylindrical autoclave of stainless-steel, 350.0 mm height, 60.0 mm inner diameter and 120.0 mm outer diameter. The sample was loaded from the bolt-hole into the autoclave, and the hole was plugged with a screw bolt after each run. The experiments have been carried out at 493, 523 and 593 K, and with molar ratios of 1:6–1:40 of the beechnut oil to methanol. Nominal transesterification reaction time was 15 min. The autoclave was put vertically in into a furnace maintained at desired temperature for a set time and provided with an electrical heating system power source, with changing heating rates and power was adjusted to give an approximate heating time of 25 min. After completion of the reaction, the reactor was immersed in a cold water bath to stop the reaction. The variation of temperature in the system was controlled with ±2 K.

In a typical run, the autoclave is charged with beechnut oil (max. 125 g) and methanol (max. 250 g) with changed molar ratios. After each run, the autoclave is cooled, and the autoclave is poured into a collecting vessel. All the rest of the contents are removed from the autoclave by washing with methanol. A successful transesterification reaction produces two liquid phases: ester and crude glycerin. Washing the ester is a two-step process, which is carried out with extreme care. A water wash solution at the rate of 28% by volume of oil and 1 g of tannic acid per liter of water is added to the ester and gently agitated. Air is carefully introduced into the aqueous layer while simultaneously stirring very gently. This process is continued until the ester layer becomes clear. After settling, the aqueous solution is drained and water alone is added at 28 percent by volume of oil for the final washing (Babu and Chaurasia, 2003; Demirbas, 2008d).

2.6. Viscosity, density and flash point measurements

Each sample of biodiesel was used for viscosity, flash point and density measurements. The kinematic viscosity measurements were carried out as mm^2/s (cSt) at 311 K temperature according to ASTM D445 standard method. The temperatures were checked with a digital thermometer within the thermostat and the viscosimeter (Demirbas, 2003). The flash point was measured by using an automatic Pensky–Martens flash point tester. The density of biodiesel was directly measured by a simple lab hydrometer at different temperatures.

3. Results and discussions

The fatty acid compositions of the beechnut and beech wood oils are listed in Table 1. The average fatty acid compositions of beechnut and beech wood oils are considerably different (Table 1). Oleic (18:1) and linolenic acid (18:3) contents of beechnut and beech wood oils are very different. The beech wood oil has higher linolenic acid and it is a drying oil.

The yield of bio-char was calculated from the ash yields of the bio-char and biomass (Zanzi et al., 1996):

$$\text{Bio-char yield (wt\% daf)} = \frac{(ab/ac) - (ab/100)}{1 - (ab/100)} \times 100 \tag{4}$$

where ab is wt% ash in dry biomass, and ac is wt% ash in dry bio-char.

Table 2 shows the effect of temperature on the bio-char yield. The bio-char yield decreases from 25.4 wt% to 13.8 wt% for particle size between 0.8 mm and 1.2 mm when the temperature is increased from 950 to 1250 K (Table 2).

Table 1 – Average fatty acid compositions of beech wood and beechnut oils (% by weight).

Oil	16:0	16:1	18:0	18:1	18:2	18:3	Others
Beechnut	8.8	0.1	3.2	30.3	48.7	0.2	6.3
Beech wood	11.6	3.5	4.2	10.4	37.3	23.4	11.6

Table 2 – Effect of temperature on bio-char yield (wt% daf) (particle size: 0.8–1.0 mm).

Temperature (K)	950	1050	1150	1259
Yield of bio-char (wt%)	25.4	21.6	17.3	13.8

Table 3 – Effect of particle size on bio-char yield (wt% daf) (final temperature: 950 K).

Particle size (mm)	0.4	0.6	0.8	1.0	1.2
Yield of bio-char (wt%)	17.6	19.5	23.6	25.4	26.5

Table 4 – Effect of temperature on carbon content of bio-char yield (particle size: 0.8–1.0 mm).

Temperature (K)	950	1050	1150	1250
Carbon content of bio-char (wt%)	81.7	85.8	89.1	92.5

Table 5 – Chemical and structural analyses of beech wood.

Analysis	wt%
Elemental analysis (dry ash free basis)	
Carbon	49.5
Hydrogen	6.2
Nitrogen	0.4
Oxygen (by different)	41.2
Structural analysis (dry ash free basis)	
Hemicelluloses	31.2
Cellulose	45.3
Lignin	21.9
Alcohol/benzene (1/1, v/v) extractives	1.6
Proximate analysis	
Ash	0.4
Volatile matter	82.5
Fixed carbon	17.1

Table 3 shows the effect of particle size on bio-char yield in the conditions selected for the study. In the experiments with beech wood at 950 K, the bio-char yield decreases from 22.7 wt% to 16.8 wt% when the particle size is reduced from 1.2 mm to 0.4 mm.

Table 4 shows the effect of temperature on carbon content of bio-char. The carbon content of bio-char increases from 81.7% to 92.5% with increasing of temperature from 950 K to 1250 K (Table 4). During secondary carring, oxygen and hydrogen compounds with volatile materials are released. Meanwhile, it is a little carbon loss from unreacted solid residue (Eqs. (1)–(3)). However, as a result, the percentage of carbon is increasing.

Table 5 shows the chemical and structural analyses of beech wood. The yields of fractions from the alkali liquefaction products of beech wood are given in Table 6. Table 6 shows that within the range of 553–573 K, beech wood was converted completely into a liquid product and the yield of total water insolubles were about 66% in the presence of 10% of sodium carbonate as alkali. At these conditions the yields of non-condensed gaseous materials were almost negligible. Since water in the reaction medium has led to foaming it was removed continuously from the medium.

Table 6 – Yields of fractions from the alkali (8% Na_2CO_3 of the sample) glycerol liquefaction products of beech wood.

Product	% of used sample
Total water soluble materials	34.5
Total water insoluble materials	65.5
Tarry materials	37.8
Ether extractables	9.1
Benzene extractables	18.6

Table 7 – Saponification value, iodine value and higher heating value (HHV) of oils (% by weight).

Oil	Saponification value (SV)[a]	Iodine value (IV)[b]	HHV (MJ/kg)
Beechnut	193.5	110.6	39.8
Beech wood	202.2	105.2	39.6

[a] SV: mg KOH/g oil.
[b] IV: g I/100 g oil.

Well-ripened beechnut (called also mast/beechmast) yields from 16 to 23% of non-drying oil. Beechnuts are known to yield oil by the usual methods of extraction.

Beechnuts are known to yield oil by the usual methods of extraction. Well-ripened beechnut (called also mast/beechmast) yields from 16 to 23% of non-drying oil.

Table 7 shows some physico-chemical properties of beechnut and beech wood oils such as saponification value, iodine value and higher heating value.

Table 8 shows the fuel properties of diesel fuel and biodiesel from beechnut oil. The kinematic viscosity of diesel fuels varies from as low as 1.3 mm^2/s (=cSt) to as high as 4.1 mm^2/s and kinematic viscosity of biodiesel from beechnut oil varies from 3.8 to 4.0 mm^2/s (measured at 313 K).

The viscosity of biodiesel is very important, because this property affects pump and pipeline sizing and operating temperature. Most importantly, the oil viscosity has a significant effect on the atomization quality of spray injectors and the diameter of the fuel droplet from the injector (Allen et al., 1999). Viscosity influences on the burning performance directly and engine life in long term (Lee et al., 2002; Kerschbaum and Rinke, 2004), flame length, combustion efficiency (carbon burnout), and emissions (Shaddix and Hardesty, 1999). Since the volume of biodiesel slightly changes with temperature, the viscosity and density depends on the temperature of biodiesel.

3.1. *Liquefaction in alkaline glycerol*

Fig. 3 shows the plot for liquefaction yield of beech wood versus temperature in glycerol and alkali (8% Na_2CO_3 of used sample) glycerol. As can be seen from Fig. 3, temperature appeared to have no significant effect within the range of 520–540 K, it has been shown that application of temperature below 530 K gives just a solid residue rather than a liquid product. Beech wood was partly converted to liquefaction products in glycerol without alkali.

Alkaline degradation of whole biomass or of its separate structural components (cellulose and lignin) leads to a very complex mixture of chemical products. In turn, these compounds, due to their greater variance in structure, must involve extensive and complex mechanistic pathways for their production (Demirbas, 2000b). The degradation process cannot be within the 410–430 K for the rate of degradation appears very slow in this temperature range. Qualitative observations also indicated that the cellulose produced at above 480 K was darker than that produced at 440 K. The yield of total

Table 8 – Fuel properties of diesel fuel and biodiesel from beechnut oil.

Property	Test method	ASTM D975 (diesel)	ASTM D6751 (biodiesel, B100)
Flash point	D 93	325 K min	446 K
Density (at 289 K)	D 941-88	850 max kg/m^3	876 kg/m^3
Water and sediment	D 2709	0.05 max vol.%	0.03 vol.%
Kinematic viscosity (at 313 K)	D 445	1.3–4.1 mm^2/s	3.8–4.0 mm^2/s
Sulfated ash	D 874	0.02 max wt%	–
Ash	D 482	0.01 max wt%	–
Sulfur	D 5453	0.05 max wt%	–
Sulfur	D 2622/129	0.05 max wt%	–
Copper strip corrosion	D 130	No. 3 max	No. 2
Cetane number	D 613	40 min	49
Aromaticity	D 1319	35 max vol.%	–
Carbon residue	D 4530	0.05 max wt%	0.02
Carbon residue	D 524	0.35 max mass%	–
Distillation temp. (90% volume recycle)	D 1160	555 K min–611 K max	–

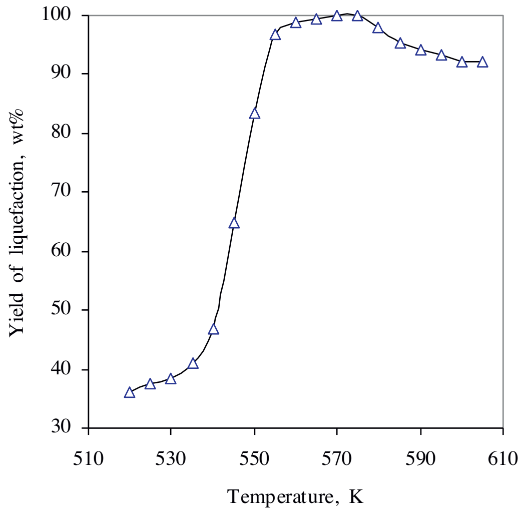

Fig. 3 – Plots for liquefaction yield of beech wood versus temperature in alkali (8% Na_2CO_3 of used sample) glycerol. Particle size: 0.12–0.40 mm.

degradation increases with increasing reaction temperature (Demirbas, 2000a).

3.2. *Bio-oil via pyrolysis*

Pyrolysis is becoming an increasingly popular option for converting biomass to bio-oil, charcoal, and gaseous fuels. The literature on pyrolysis of biomass to produce pyrolytic oils is vast and is summarized in several review articles (Karaosmanoglu et al., 1999; Demirbas and Arin, 2002; Demirbas, 2002b, 2005, 2006, 2008d; Bridgwater, 2003; Yaman, 2004; Madras et al., 2004; Knothe, 2005; Knothe and Steidley, 2005; Minami and Saka, 2006; He et al., 2007; Tekin et al., 2013). The liquid or oil fraction is commonly called pyrolytic oil or bio-oil. Slow pyrolysis, which employs lower process temperatures and longer reaction times, favors charcoal production (Demirbas and Arin, 2002).

Fig. 4 shows the plots for yield of liquid products from pyrolysis versus pyrolysis temperature for different particle size of beech wood. From Fig. 4, increases of liquid yields are considerably sharply for all of the samples with increasing of pyrolysis temperature from 690 K to 720 K. The highest increase of bio-oil yield was obtained from the beech wood sample with +0.20 mm particle size in the pyrolysis conditions. The maximum bio-oil yield was 35.8% at 720 K.

Bio-oil from wood pyrolysis is typically a liquid, almost black through dark red brown. The density of the liquid is about 1200 kg/m^3, which is higher than that of fuel oil and significantly higher than that of the original biomass. Bio-oils typically have water contents of 14 to 33 wt%, which cannot be removed by conventional methods like distillation. Phase separation may occur above certain water contents (Demirbas, 2008d).

The liquid fraction of the pyrolysis products consists of two phases: aqueous and non-aqueous phases. Aqueous phase contains a wide variety of organo-oxygen compounds of low molecular weight. Among of the liquid products, methanol is one of most valuable products. Non-aqueous phase contains insoluble organics of high molecular weight (Demirbas, 2000b, 2002b). This phase is called as tar and is the product of greatest interest. Tar from wood is a very complex body, its composition varying with the kind of wood and method of preparation. The chief constituents are pyrocatechol, phenol, guaiacol, cresol, creosol, methyl-creosol, phlorol, toluene, xylene, naphthalene, and other hydrocarbons (Demirbas, 2000a, 2000b). The ratios of acetic acid, methanol, and acetone of aqueous phase were higher than those of non-aqueous phase. Tar a viscous black fluid that is a byproduct of the pyrolysis of beech wood

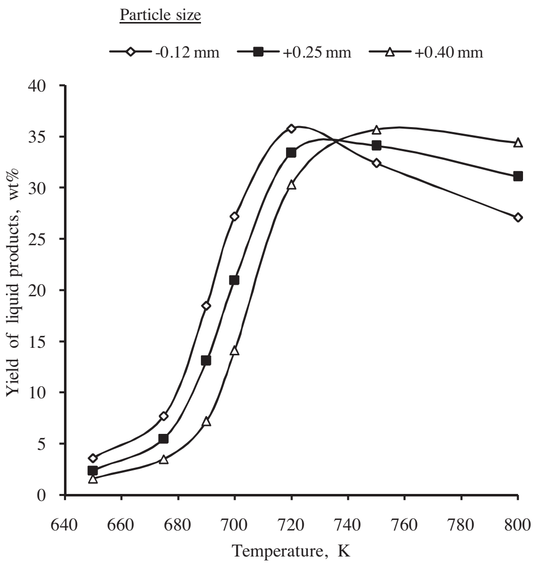

Fig. 4 – Plots for yield of liquid products from pyrolysis versus pyrolysis temperature for different particle sizes of beech wood.

and is used in pitch, varnishes, cements, preservatives, and medicines as disinfectants and antiseptics.

3.3. *Conversion of beechnut oil into biodiesel in compressed methanol*

Fig. 5 shows the plots of conversion into methyl ester or the yield of methyl ester as treated with subcritical (at 493 K) and supercritical (at 523 and 593 K) methanol as a function of reaction time for the beech wood oil. It is evident that at subcritical state of the alcohol, reaction rate is so low and gradually increased as either pressure or temperature rises. The critical temperature and the critical pressure of methanol are 512.4 K and 8.0 MPa, respectively. It was observed that increasing the reaction temperature, especially to supercritical conditions, had a favorable influence on the methyl ester conversion. The effect of temperature and reaction time on the conversion of oil to methyl esters was studied keeping the oil to methanol molar ratio fixed at 1:40 varying the temperature from 493 to 593 K. More recently, it has been observed that one of the attractive characteristics of biodiesel supercritical method is the low reaction time (He et al., 2007). In the first, Saka and Kusdiana (2001a) obtained a conversion in methyl esters as high as 95 wt% in about 4 min of reaction in a batch reactor.

Fig. 6 shows the plots of conversion into methyl ester or the yield of methyl ester as treated with subcritical (at 493 K) and supercritical (at 523 and 593 K) methanol as a function of reaction time for the beechnut oil. Transesterification behaviors of both oils are considerably different. When the conversion was increased from 28.4 to 61.7% for beech wood oil, the conversion was increased from 33.2% to 65.7% for beechnut oil with molar ratio of the oil to methyl alcohol was 1:40 at 493 K for 11 min. When the conversion was increased from 61.6 to 95.6% for beech wood oil, the conversion was increased from 68.7% to 97.3% for beechnut oil with molar ratio of the oil to methyl alcohol was 1:40 at 593 K for 11 min.

The conversion degree of oil depends on its fatty acid composition (Knothe, 2005; Knothe and Steidley, 2005). The conversion degrees increase with increasing of the saturated fatty acid triglyceride content. For the same set, this also can be looked as a decrease in the conversion degrees with an increase in the diunsaturated (linoleic) acid content. One can also compare the conversion degrees of beechnut oil and beech wood oil. Both have similar diunsaturated acid content but because beechnut oil has less saturated acids and more mono-unsaturated acid, the conversion degree of beech wood oil is lesser than that of beechnut oil. From Table 1, the beech wood oil, which contains the highest amount of triunsaturated acid (linolenic), has slower conversion degree. As a result, oils that contain triglycerides of triunsaturated fatty acids will transesterify the slowest compared to triglycerides of diunsaturated or monounsaturated fatty acids, whose reaction rates would be slower than that of triglycerides of saturated fatty acids.

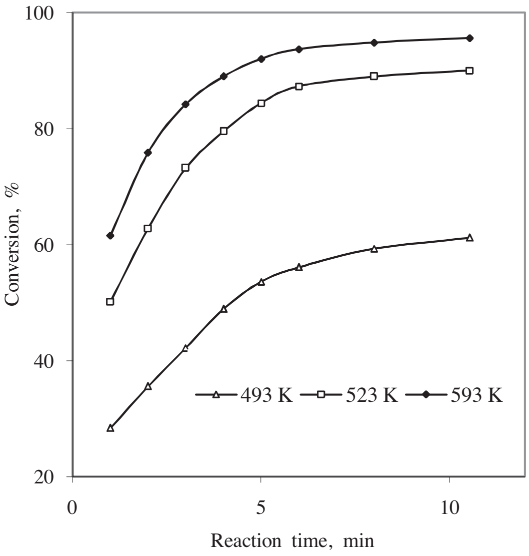

Fig. 5 – Plots of conversion as treated with subcritical (at 493 K) and supercritical (at 523 and 593 K) methanol as a function of reaction time for beech wood oil. Molar ratio of beech wood oil to methyl alcohol: 1:40.

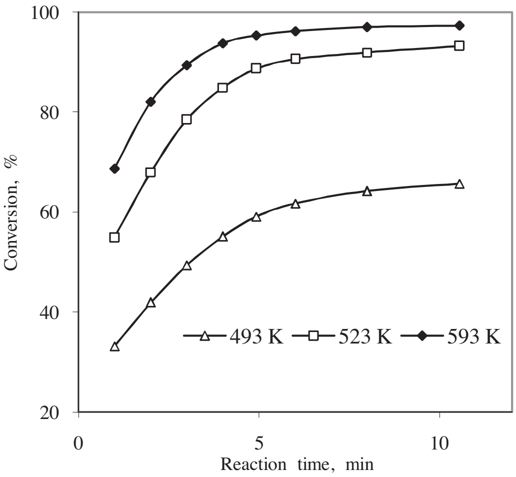

Fig. 6 – Plots of conversion as treated with subcritical (at 493 K) and supercritical (at 523 and 593 K) methanol as a function of reaction time for beechnut oil. Molar ratio of beechnut oil to methyl alcohol: 1:40.

It was reported that 623 K was the best temperature to carry out reactions in batch mode with methanol as solvent (Madras et al., 2004). However, high temperature values (>625 K) can favor backward reaction of glycerol with ethyl esters and may cause products degradation, thus decreasing the production of fatty acid esters (Madras et al., 2004; Minami and Saka, 2006).

The molar ratio of methanol to oil is one of the most important variables influencing the conversion into methyl esters. The effect of molar ratio was investigated at 593 K and 11 min. Fig. 7 shows the effect of the molar ratio on the yield of methyl ester for the beechnut oil to methanol in supercritical methanol. The beechnut oil was transesterified at 1:1, 1:20 and 1:40 oil–methanol molar ratios in at 593 K. In 1:1 oil–methanol molar ratio the yield of methyl ester is considerably lower. It was observed that the yield of methyl ester increased with increasing the oil–methanol molar ratio. When the molar alcohol ratio was increased from 20:0 to 40:0, the yield of methyl ester increased from 89.3% to 97.43%.

After a certain period of transesterification time values of the molar ratio of methanol to oil affect better conversions in shorter reaction times. This indicates that the higher molar ratio of methanol/ethanol results in better transesterification, perhaps due to the increased contact area between methanol and triglycerides (Demirbas, 2006). The results obtained shows good agreement with previous work, where maximum conversion was obtained for rapeseed oil (Demirbas, 2006) at molar ratio of 42:1, for various vegetable oils (Diasakov et al., 1998;

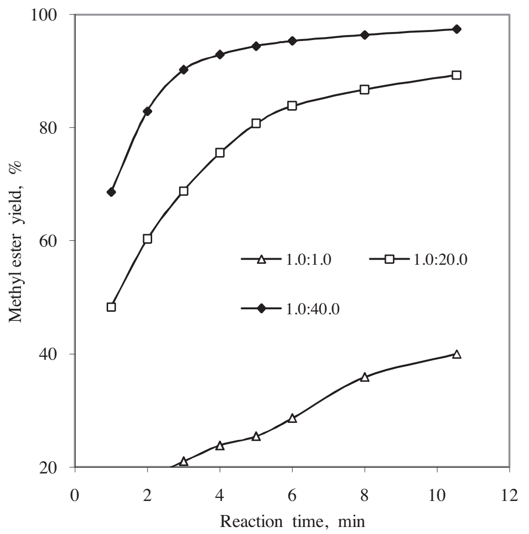

Fig. 7 – Effect of molar ratio of beechnut oil to methanol on yield of methyl ester at 593 K.

Ma et al., 1999; Demirbas, 2002c) at molar ratio of 41:1 and for linseed oil at a molar ratio of 40:1.

The supercritical methanol process, compared with the conventional method, is non-catalytic, much simpler for purification, lower reaction time and higher yield of methyl ester (Demirbas, 2002c; Meher et al., 2006). Therefore, the supercritical methanol method would be more effective and efficient than the common commercial process (Kusdiana and Saka, 2004).

The conversion of oil into methyl esters conversion was found to increase significantly in supercritical methanol. In addition, in the conventional transesterification of fats/vegetable oils for biodiesel production, the presence of free fatty acids and water causes soap formation, consumes catalyst and reduces catalyst effectiveness, resulting in a low conversion (Komers et al., 2001). Synthesis in supercritical methanol was not affected by presence of water and free fatty acids (Kusdiana and Saka, 2004). Transesterification in supercritical methanol require no catalyst and the purification of products after transesterification is much simpler compared with the conventional commercial method in which all the catalyst and saponified products have to be removed from biodiesel fuel.

4. Conclusion

Oriental beech wood has subjected to carbonization, liquefaction and pyrolysis obtained for biochar, bio-oils and gaseous products. Oriental beech wood was liquefied in glycerol in the presence of Na_2CO_3 as alkali. Alkali salts can lead to the formation of hydrolysis of macromolecules, such as cellulose and hemicelluloses, into smaller fragments.

In beech wood-derived pyrolysis oil or bio-oil, specific oxygenated compounds are present in relatively large amounts. The liquid fraction of the pyrolysis products consists of two phases: aqueous and non-aqueous phases. Aqueous phase contains a wide variety of organo-oxygen compounds of low molecular weight.

The beechnut oil was converted to biodiesel in supercritical methanol without using the catalyst. Biodiesel is a diesel replacement and renewable fuel that is manufactured from plant oils and animal fats. Transesterification reaction of beechnut oil in supercritical methanol was investigated without using the catalyst. The vagetable oils were transesterified 1:6–1:40 vegetable oil/alcohol molar ratios in catalytic and supercritical methanol conditions. In the supercritical methanol transesterification method, the yield of conversion raises 70–95% for first 10 min.

The most important variables affecting the methyl ester yield during transesterification reaction are molar ratio of alcohol to vegetable oil and reaction temperature. Higher molar ratios result in greater ester production in a shorter time. It was observed that increasing the reaction temperature, especially to supercritical temperatures, had a favorable influence on ester conversion.

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